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A high resolution x-ray photoemission spectrometer has been purchased for study of the chemistry of vapor phase lubricants and new tribological materials such as quasicrystals. Typical vapor phase lubricants are compounds such as tricresylphosphate which react with iron surfaces to form lubricating films at high temperatures. Understanding the mechanism by which they decompose on surfaces to form these films is central to developing new VP lubricants or improving the performance of existing VP lubricants. Because of their complexity, high resolution spectroscopy is needed to follow the course of their reactions on surfaces. Quasicrystals are also materials which have potential for use as low friction coatings at high temperatures. These are complex alloys with three or more components which, because of their complexity would benefit from study using high resolution XPS. Understanding the kinetics of their oxidation is important to understanding their performance as high temperature oxidation resistant low friction coatings. The XPS equipment needed for these studies has been purchased and a new ultra-high vacuum chamber is being constructed to house the components of this spectrometer.

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High Resolution XPS Analysis of New Lubricants and Materials for Tribology under Extreme Conditions

Grant No. AFOSR-F49620-00-1-0200
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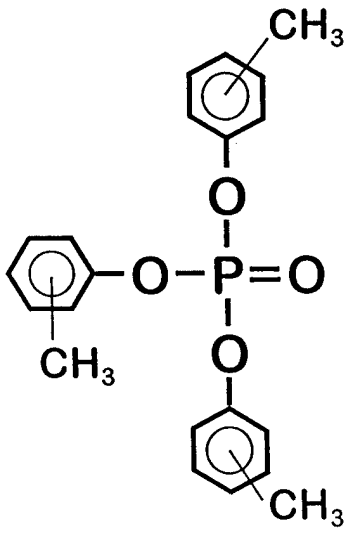
Summary

A high resolution x-ray photoemission spectrometer has been purchased for study of the chemistry of vapor phase lubricants and new tribological materials such as quasicrystals. Typical vapor phase lubricants are compounds such as tricresylphosphate which react with iron surfaces to form lubricating films at high temperatures. Understanding the mechanism by which they decompose on surfaces to form these films is central to developing new VP lubricants or improving the performance of existing VP lubricants. Because of their complexity, high resolution spectroscopy is needed to follow the course of their reactions on surfaces. Quasicrystals are also materials which have potential for use as low friction coatings at high temperatures. These are complex alloys with three or more components which, because of their complexity would benefit from study using high resolution XPS. Understanding the kinetics of their oxidation is important to understanding their performance as high temperature oxidation resistant low friction coatings. The XPS equipment needed for these studies has been purchased and a new ultra-high vacuum chamber is being constructed to house the components of this spectrometer.

Project Objectives

The research program in the P.I.'s laboratory is focused on surface science and surface chemistry problems in tribology. The equipment purchased with the funds provided for this project will be integrated into this program and will enhance the overall capabilities of the P.I.'s laboratory. A central feature of the laboratory is instrumentation for measuring the frictional forces between well defined single crystalline surfaces. In additional the lab has many types of spectroscopic tools for surface analysis and for the study of lubricant surface chemistry. The new instrumentation consists of a monochromated x-ray source and a highly sensitive hemispherical electron energy analyzer. Although low resolution x-ray photoemission is already available, the instrumentation purchased with these funds will allow us to obtain high-resolution x-ray photoemission spectra of complex lubricants molecules.

One of the problems under current investigation in the lab is the surface reaction mechanism of vapor phase lubrication (VPL). Vapor phase lubrication is used under extreme conditions in situations where the temperatures are too high to allow the use of traditional lubricant fluids. The most commonly studied VP lubricant is tricresylphosphate (TCP) shown below.



TCP reacts on Fe surfaces to form a thin film of polyphosphate glass with embedded carbon. The mechanism of this reaction of TCP and other phosphates determines their

relative abilities to serve as vapor phase lubricants. Ongoing work in the P.I.'s lab has explored this reaction mechanism in order to determine the initial step. This depends on the nature of the phosphate. In the case of the aryl phosphates the initial step appears to be cleavage of the P-O bond to produce an aryloxy group on the surface. The subsequent decomposition of this aryloxy group results in the deposition of carbon onto the surface. High resolution XPS will enable us to examine this reaction and the kinetics of this step more accurately.

The quasicrystals are complex ternary or higher order alloys that have structures with five-fold, ten-fold, and other unusual rotational symmetry elements. These structures are non-periodic but nonetheless well ordered. It is expected that as a consequence, they have many unique properties that differentiate them from common materials with periodic structures. One such property is low friction. This has been proposed to arise from the fact that no two quasicrystal surfaces can come into commensurate contact with one another. Alternately, it may be a consequence of their high hardness which in turn may be a consequence of their quasicrystalline structure. The first measurements of friction between truly clean surfaces of quasicrystals were made in the P.I.'s laboratory. These have shown that the frictional properties of these surfaces are sensitive to the presence of contamination. A systematic study showed that the growth of thin oxide films on the quasicrystal surfaces resulted in a decrease in the friction between them. The oxide film appears to be formed predominantly of Al_2O_3 which grows in the presence of O_2 to a thickness which the passivates the surface against further oxidation. The use of a high resolution x-ray photoemission spectrometer will enable us to study both the kinetics and the initial mechanism of the formation of these thin passivating films.

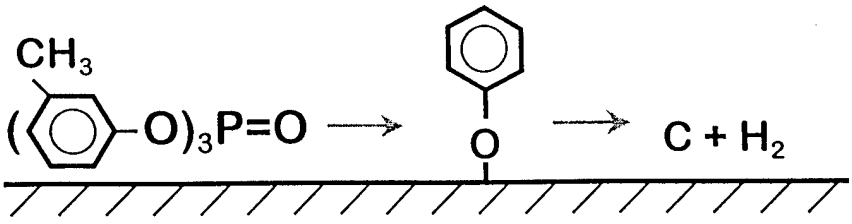
The UHV chamber that is being prepared for the high resolution XPS system will have all the instrumentation for surface preparation and for surface analysis that will be needed for the study of both the vapor phase lubricants or the quasicrystals. A schematic of the system is shown in figure 1. The apparatus has three levels on which surface preparation and analysis can be performed. A manipulator translates the samples between the three levels and allows both heating and cooling of the sample between 100 K and 1200K. The upper level of the apparatus is devoted to the instrumentation for the high resolution XPS, housing both the monochromated x-ray source and the

hemispherical electron energy analyzer. The middle level is to be used for sample preparation using ion sputtering and annealing. This level will also be used for the adsorption of VP lubricants onto the surface or for exposure of the quasicrystal surfaces to oxidation. Finally, the middle level houses a quadrupole mass spectrometer which is used to obtain thermal desorption spectra from the surface. At the lowest level of the chamber is a small UHV cell that is used for infra-red reflection absorption spectroscopy. This can be used to obtain vibrational spectra of the materials on the sample surface.

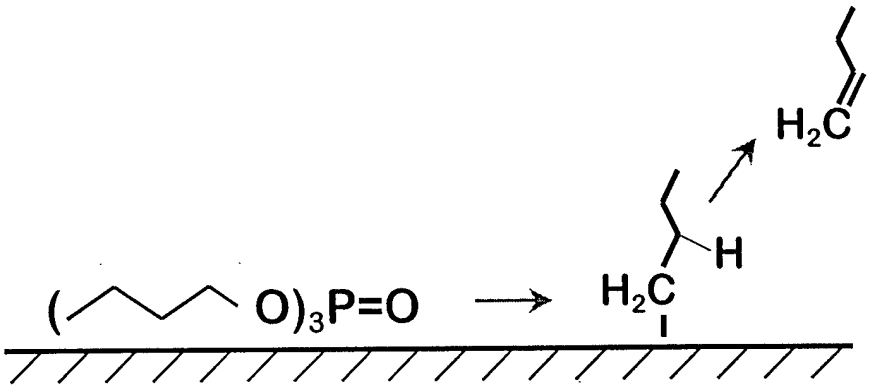
Technical Progress and Accomplishments

The principle efforts on the project to date have involved the design of the chamber to house the high resolution XPS systems and the purchasing of the equipment. At this point in time the chamber is being constructed, the analyzer has been received and the monochromated x-ray source is in transit. Once all the components are in place the system will be assembled and tested. This is expected to take place over the coming summer months.

In the meantime, significant progress has been made on the scientific components of the project. Our studies of vapor phase lubrication have progressed from using small model compounds to study VPL to the point of using TCP itself adsorbed on the surface of Fe films. As predicted on the basis of our previous studies of the model compound trimethylphosphite (TMP) we find that the initial reactions of these compounds with the Fe surface are through cleavage of either the C-O or the P-O bonds. In the case of the arylphosphates such as TCP the initial step is cleavage of the P-O bond to produce adsorbed aryloxy groups. These decompose to deposit large amounts of carbon on the Fe surface along with phosphorus and oxygen.



In contrast the alkylphosphates such as tributylphosphate (TBP) decompose by C-O bond cleavage to produce adsorbed alkyl groups. These alkyl groups are poor at depositing carbon on to the Fe surface because they can react by β-hydride elimination to produce olefins which then desorb from the surface.



We have proposed that β-hydride elimination, which occurs in the case of the alkyl groups but not in the case of aryl groups, is the root cause of the difference in the efficiency of the alkyl and aryl phosphates as VP lubricants.

Our study of the tribological properties of quasicrystals has made use of thin film samples of AlCuFeCr provide by TAT Inc. These have been studied using low resolution XPS and UHV friction measurements. As in the case of the previously studied AlPdMn quasicrystals we find that the frictional properties of the AlCuFeCr surfaces are very sensitive to low levels of contamination. The surfaces as received have been shown to be covered with a passivating film of Al_2O_3. Finally, we have observed that the frictional properties of these materials show some interesting temperatures dependence with a minimum in the friction between the surfaces occurring at 500K. This suggests that they may be particularly useful at high temperatures.

Work on both the projects is ongoing and is making use of the existing apparatus in the laboratory. Once the new apparatus is fully constructed and in service the its high resolution XPS capabilities will greatly enhance the quality of the data that is being obtained.

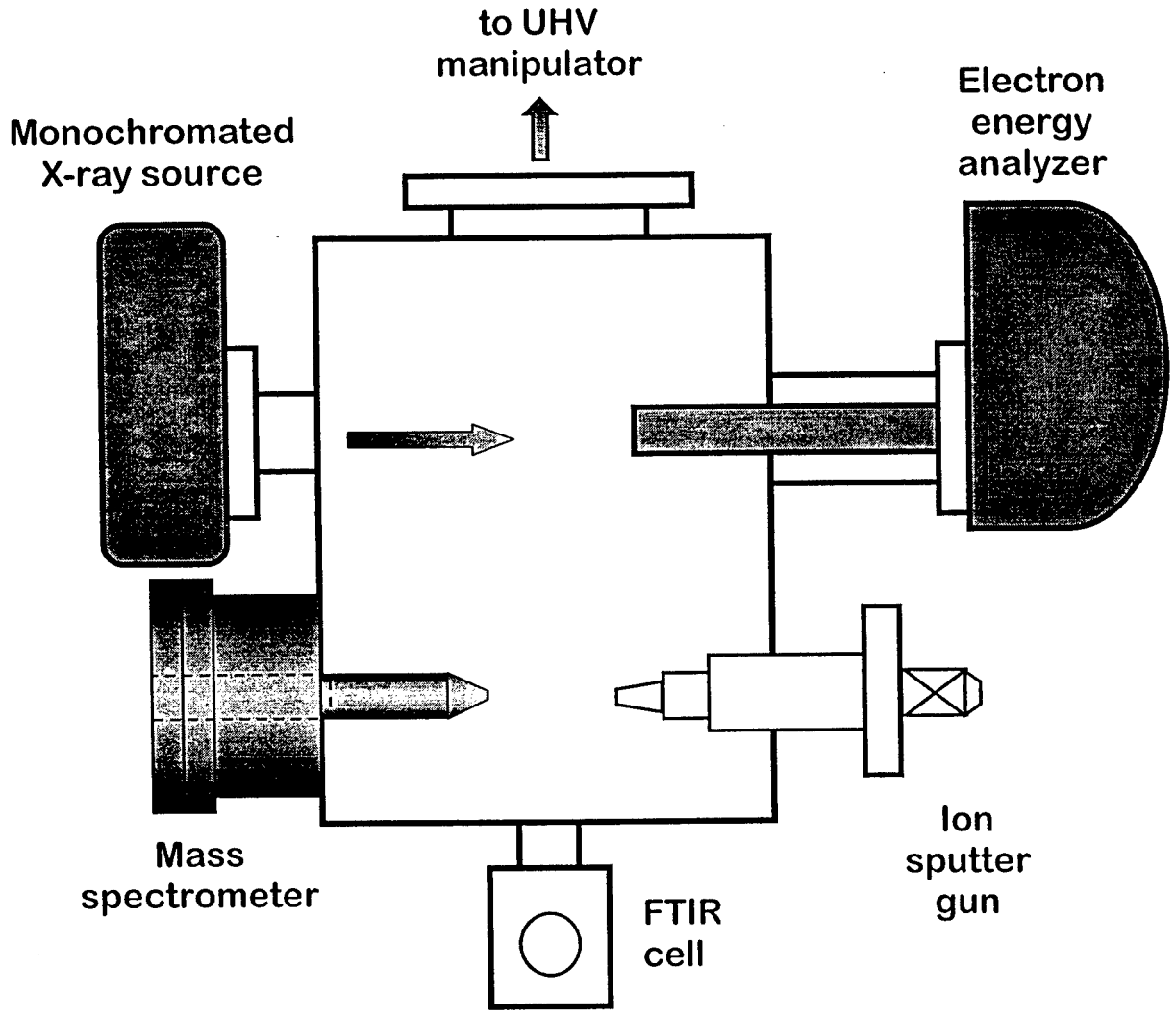


Figure 1. Schematic drawing of the UHV chamber under construction for the high resolution x-ray photoelectron spectrometer. The chamber has three levels for sample preparation and analysis. The new high resolution XPS instrumentation is housed in the upper level.

Equipment Purchases:

1. Specs Phobios 150 MCD Analyzer	89,282
2. VG monochromated x-ray source	87,600
3. VG X-ray Power Supply	12,000
Total	$188,882